FORMULATION AND CHARACTERIZATION OF LIGNIN-PHENOL-FORMALDEHYDE RESINS FOR PLYWOOD

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FORMULATION AND CHARACTERIZATION OF LIGNIN-PHENOL-FORMALDEHYDE RESINS FOR PLYWOOD

by

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS

%	Percent
±	Plus minus
Δ	Delta
µ	Micro
µl	Microliter
µm	Micrometer
1^{st}	First
2^{nd}	Second
3^{rd}	Third
4^{th}	Forth
5^{th}	Fifth
A	Absorbance
C	Carbon
cm	Centimetre
cm^{-1}	Per centimeter
g	Gram
g/cm^3	Gram per centimeter cube
g/m^3	Gram per meter cube
g/ml	Gram per mililiter
g/mol	Gram per mol
h	Hours
kg/m^3	Kilogram per meter cube
kgf/cm^2	Kilogram feet per centimetre square
kN/min	Kilo newton per minute
L	Liter

m	Meter
M	Molar
mg ml^{-1}	Miligram per mililiter
mg	Milligram
MHz	Mega hertz
min^{-1}	Per minute
mins	Minutes
ml	Millilitre
mm	Milimeter
mmol/g	millimol per gram
M_n	Number-average molecular weight
mol/L	Mol per litre
MPa	Mega pascal
mPa.s	miliPascal second
M_w	Weight-average molecular weight
N	Nitrogen
N/mm^2	Newton per milimeter square
o	Ortho
O	Oxygen
P	Phenol
^oC	Degree Celcius
S	Sulphur
T	Temperature
T_g	Transition temperature
T_o	Onset temperature
T_p	Peak temperature
V	Volume
v/v	Volume per volume
w/w	Weight per weight
α	Alpha
β	Beta

ABBREVIATIONS

^{1}H-NMR	Proton Nuclear Magnetic Resonance
^{13}C-NMR	Carbon-13 Nuclear Magnetic Resonance
CBR	Cyclic boil resistant
$CDCl_3$	Deuterated chloroform
CPF	Commercial phenol formaldehyde
DBE	Double bond equivalent
DMSO-$_{d6}$	Deuterated dimethysulfoxide
DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetric
EFB	Empty fruit bunch
F	Formaldehyde
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
G-type	Guaicyl type
H	Hydrogen
HCl	Hydrochloric acid
HPLC	High Performance Liquid Chromatography
INT	Interior
KBr	Potassium bromide
Lig	Lignin
LPF	Lignin-phenol-formaldehyde
MR	Moisture resistance
NaOH	Sodium hydroxide
OLPF	Optimum lignin-phenol-formaldehyde
OPEFB	Oil palm empty fruit bunch
PBF	Pentaflourobenzaldehyde

PF	Phenol formaldehyde
POME	palm oil mill effluent
SEM	Scanning Electron Microscope
SFF	saccharification and fermentation process
S-type	Syringyl type
TGA	Thermogravimetric Analysis
THF	tetrahydrofuran
UV	Ultraviolet
WBP	weather and boil point

FORMULASI DAN PENCIRIAN RESIN LIGNIN-FENOL-FORMALDEHID UNTUK PAPAN LAPIS

ABSTRAK

Formaldehid fenol merupakan salah satu perekat kayu utama yang digunakan dalam industri kayu. Bahan mentah perekat ini diperolehi daripada minyak petroleum. Sejak kebelakangan ini, peningkatan harga petrokimia menjadikan penukargantian bahan ini dengan sumber semula jadi sangat diperlukan. Dalam kajian ini, penggantian fenol dalam penghasilan perekat fenolik dengan menggunakan lignin yang diekstrak dari sisa kelapa sawit telah diterokai. Lignin kraft dan lignin soda telah dicirikan dari segi sifat kimia dan sifat terma untuk menentukan kesesuaian dan potensinya bagi penggabungan separa ke dalam resin formaldehid fenol. Parameter bagi penyediaan formula resin lignin-fenol-formaldehid (LPF) seperti peratusan lignin, nisbah molar formaldehid/fenol, nisbah mangkin dan tempoh masa tindak balas telah dioptimakan. LPF yang optima (OLPF) telah dibandingkan dengan PF komersial (CPF) dari segi sifat, kimia, haba dan mekanik. Daripada analisis yang dilakukan, lignin kraft telah menunjukkan potensi yang amat besar kerana mempunyai kandungan kumpulan fenolik hidroksil yang lebih tinggi berbanding dengan lignin soda. Parameter optima bagi menghasilkan formulasi baru LPF boleh dicapai dengan penggantian 50% fenol dengan lignin, menggunakan nisbah molar formaldehid/fenol sebanyak 2.0, nisbah mangkin sebanyak 0.6 dan tempoh tindak balas selama 4 jam. Perekat LPF telah dicirikan untuk sifat fizik, kimia, terma dan mekanikal. Perbandingan resin ini menunjukkan bahawa

OLPF adalah setanding dengan CPF. Walaupun kekuatan kericihan dan peratus kegagalan kayu bagi CPF adalah lebih tinggi sedikit daripada OLPF, OLPF masih memenuhi keperluan piawai.

FORMULATION AND CHARACTERIZATION OF LIGNIN-PHENOL-FORMALDEHYDE RESINS FOR PLYWOOD

ABSTRACT

Phenol formaldehyde is one of the main wood adhesive used in wood industry. The raw material of this adhesive is derived from petroleum oil. In recent years, the increasing price of petrochemical makes its replacement by natural resources become indispensible. In this study, the possibility of substituting phenol in phenolic adhesive production with lignin which was extracted from oil palm waste was explored. Kraft and soda lignins were characterized in terms of chemical and thermal properties to determine their suitability and potential for partial incorporation into phenol formaldehyde resin. The parameters for preparation of lignin-phenol-formaldehyde (LPF) formulation resin such as lignin percentage, formaldehyde/phenol molar ratio, catalyst ratio and reaction duration were optimized. The optimum LPF (OLPF) was compared with the commercial LPF (CPF) in terms of chemical, thermal and mechanical properties. From the analyses, kraft lignin showed tremendous potential due to higher phenolic hydroxyl group content compared to soda lignin. The optimum parameters to produce the newly formulated LPF can be achieved by 50% replacement of phenol to lignin, using formaldehyde/phenol molar ratio of 2.0, catalyst ratio of 0.6 and the reaction time of 4 hours. The LPF resins were characterized for their physical, chemical, thermal and mechanical properties. Comparison of these resins shows that OLPF was comparable with CPF. Although the

shear strength and wood failure percentage of CPF was slightly higher than OLPF, the OLPF still meets the standard requirement.

CHAPTER ONE

INTRODUCTION

1.1 Background of research work

The history of wood started 3000 years ago, since the Egyptian time (Skeist and Miron, 1990; River, 1994). Wood adhesive plays an important role in wood board panels where the performance of wood panels depends on the efficiency of the adhesives. The evolution of adhesives started with the adhesives based on natural polymers such as proteins, starch and soybean. However, this type of adhesive did not meet the required bonding strength and water resistance (Pizzi and Mittal, 1994). Adhesives with low water resistance are easily attacked by fungi and micro-organisms to form mold (Lambuth, 2003), which limited their outdoor applications.

In the later years, most of the adhesive with natural resins have been replaced by synthetic resins based on formaldehyde with better strength and water resistant. These synthetic resins include urea formaldehyde (UF), phenol formaldehyde (PF), resorcinol formaldehyde (RF) and melamine formaldehyde (MF). Among these synthetic resins, PF was found to be the most popular due to their outstanding performances including excellent bonding strength, good water resistance, heat resistant and good chemical stability (Jin *et al*., 2010). However, phenol and formaldehyde used to prepare PF resins are commonly derived from non-renewable oil and natural gas which contributed to the disadvantages of toxic materials by-products and carbon dioxide emission. The environmental and health concerns due to the emission of the volatile formaldehyde and the depleting supply of petrochemicals affected the availability of the petroleum-based

adhesives (El Mansouri and Salvado, 2006). Therefore, it is essential for wood industry to develop natural renewable resources to replace these synthetic adhesives (Nadji *et al*., 2003; Khan *et al*., 2004a; Amine *et al*., 2009; Zhao *et al*., 2013a). These renewable resources offer advantages such as biodegradability, availability and lower toxicity.

Biomass is a promising source of energy which can be used to replace the fossil oil. They are cheaper than other resources, such as crude oil and natural gas (Zhang, 2008). Biomasses are organic material including plant residues (e.g. dead branches and tress), organic wastes (e.g. agricultural waste) and municipal solid waste (Demirbas, 2008). Malaysia, being the biggest producer of the oil palm has more than four million hectares of oil palm plantations. The oil palm production, such as frond, trunk, shell and empty fruit bunches yielded about 100 million tons of biomass (Malaysia Palm Oil Board 2013), as shown in Figure 1.2. Unfortunately, this oil palm biomass is treated as waste even though there are values in their components. (Mohammad Ibrahim *et al*., 2011).

(a) (b)

Figure 1.1: (a) Empty fruit bunch (EFB), (b) EFB piled up in the palm oil mill

Plant biomass, also known as lignocellulosic biomass consists of cellulose, hemicellulose and lignin (Perez *et al*., 2002). Such biomass can be used as raw materials

in some applications for the industries, due to their chemical structures, abundance and low cost. The abundance is supported by the annual production of lignocellulosic biomass worldwide, which is approximately 200 billion tonnes (Zhang, 2008). Applications using lignocellulosic biomass reduced the dependence on oil and help to reduce the emission of carbon dioxide gas in the atmosphere, which is important for sustainability. Decomposition of biomass also gave potential components, such as methanol, ethanol, phenols, substituted phenols, substituted lignins, mixed alcohols and hydrocarbons. The high content of α-cellulose in this lignocellulosic waste also makes it a viable raw material for applications in the paper manufacturing industry (Akamatsu *et al*., 1987; Khoo and Lee, 1991; Wan Rosli *et al*., 1998).

Many attempts have been conducted to utilize lignin as phenol substitute in PF adhesives. The similarities in the chemical structure and reactivity between the two polymer systems have been recognized by many studies (Nimz, 1983; Vazquez *et al*., 1995; Khan *et al*., 2004a; Khan *et al*., 2004b, Zhang *et al*., 2013a; Zhang *et al*., 2013b). This high degree of compatibility is evidenced by the fact that lignin dissolves in base or resols (alkaline phenolics) or resole-solvent systems which then reacts with formaldehyde. If the lignin OPEFB-based adhesive could be developed to meet the commercial product standard criteria, the economic potential for the chemical conversion of lignocellulosic biomass would be greatly improved. The strategy of high income, low-cost manufacturing and zero waste are the goals towards sustainability. Replacing a part of phenol in PF adhesive by lignin extracted from OPEFB waste will benefit the society by producing more environmental friendly adhesive, which indirectly support Malaysian government campaign by reutilizing the biomass from agriculture.

1.2 Problem statement

Lignocellulosic biomass is renewable natural resource that is composed mainly of organic polymers such as cellulose, hemicelluloses and lignin. There is an enormous amount of lignin produced from the pulping industry. However, most of it is treated as waste although some is burned to generate energy. Nevertheless, because of the phenolic structure of lignin, it can substitute phenol in producing PF resin. This alternative not only can reduce toxicity but also can reduce the cost of PF manufacturing. Lignin extracted from oil palm empty fruit bunch is usually obtained from soda and kraft pulping process. The variations in the raw materials and pulping process produce different lignin properties. Lignin extracted from OPEFB has low reactivity to formaldehyde. As a result, PF resin made from this type of lignin cannot be replaced with more than 10% of lignin which add difficulties to be applied in wood industry. Therefore, to fully utilize this lignin as a substitution for phenol in PF adhesives, it is necessary to optimize the process of PF resin through determination of lignin suitability. This can be done by investigating their chemical and thermal properties or by enhancing the lignin reactivity through chemical modification or by varying the parameters on adhesive formulation.

1.3 Objectives of the study

The objectives of this study are as mentioned below:

1. To characterize different types of lignin extracted from oil palm empty fruit bunch (EFB) derived from different pulping processes.

2. To use different parameter for formulating a new environmental friendly wood adhesive which require lesser usage of phenol.
3. To compare the potential of this new adhesive against the commercial resin (PF), in term of the shear test, adhesive properties testing and chemical properties.

1.4 Scopes of study

1. The recovery of soda and kraft lignin from oil palm empty fruit bunch (OPEFB) fiber *via* pulping process.
2. Characterization of soda and kraft lignin in order to investigate the suitable lignin for phenol substitution in LPF resin production by chemical, physical and thermal properties.
3. Selecting the most potential lignin between kraft and soda lignin for substituting phenol in LPF resin production.
4. Implementing chemical modification on lignin to improve the reactivity of lignin towards formaldehyde using methylolation process.
5. Formulating LPF resin with various reaction parameters such as:
    - Study on different percentage of lignin for substituting phenol in LFP adhesive: 20%, 30%, 40% and 50%
    - Study on different formaldehyde:phenol molar ratio: 1.8, 2.0, 2.2, 2.4
    - Study on different catalyst molar ratio (sodium hydroxide:lignin): 0.4, 0.5, 0.6 and 0.7
    - Study on different reaction time: 3, 4, 5 and 6 hours.

6. Characterization of newly formulated LPF adhesives in term of physical, chemical, thermal and mechanical analysis.
7. Comparison of the optimum formulated LPF adhesive and commercial PF in terms of physical, chemical, thermal and mechanical analysis.

CHAPTER TWO

LITERATURE REVIEW

2.1 Phenol Formaldehyde resin (PF)

PF was first developed by Backeland in 1907 and was first introduced as binders for particle board and plywood in 1930's (Wendler and Frasier, 1996). PF are polycondensation products from the reaction of phenol with formaldehyde, the oldest class of synthetic polymers (Pizzi, 1994; Detlefsen 2002). The tremendous research and development has significantly contributed to the chemical modification of PF properties which can be tailored for a variety of application including resins, moulding compound and wood-based composite binders (Robert, 1994). PF resins are weather durable and are commonly utilized as exterior wood-based composites (Seller, 1985). For many years, PF resin has been the preferred adhesive for bonding structural plywood.

Formaldehyde is a colorless, flammable chemical with strong odour, used in building materials and many household products. It is used in pressed-wood products such as particle board, plywood, glues, adhesives, coatings, insulation materials, industrial fungicide, germicide and disinfectant (Kopf, 2002). Formaldehyde emission results from free formaldehyde in the adhesives and from the hydrolysis of adhesives. In 1989, the U.S. Environmental Protection Agency (EPA) classified formaldehyde in high quantity or prolonged exposure as human carcinogen. The International Agency for Research on Cancer (IARC) in June 2004 has also classified formaldehyde as human carcinogen. In 2011, the National Toxicology Program, by the Department of Health and Human Services, named formaldehyde as a known human carcinogen in its

12th Report on Carcinogens. Studies conducted by the National Cancer Institute (NCI) have concluded that prolonged exposure to formaldehyde may cause leukemia in humans (Beane Freeman *et al*., 2004; Hauptmann *et al*., 2003, 2004, 2009; Pinkerton *et al*., 2004). Even with the reported studies, it is difficult to ban the use of formaldehyde in wood-based products.

Today, PF adhesive is commonly used for the exterior weather conditions. In general, more than 95% of phenol is produced from petroleum-derived benzene by the cumene process, as shown in Figure 2.1. About 35-40% of phenol is used for the production of PF (Shell Oil Report, 2014).

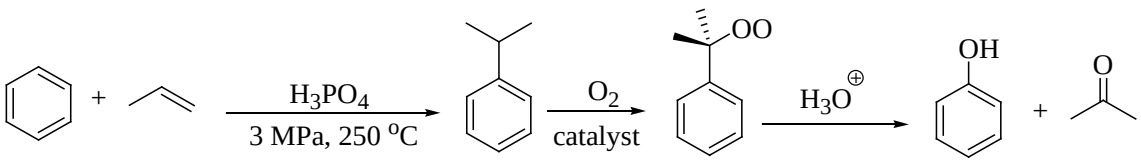

Figure 2.1: Proposed reaction pathway of phenol production.

The relatively low cost and proven performance of phenol-formaldehyde and urea-formaldehyde resins has made them the most important adhesive systems for composite wood products. Nevertheless, PF is more suitable for exterior grade compared to UF due to its moisture resistance ability. PF resin is a petroleum-based product, whereby any significant increase in the price of crude oil will affect the price of wood adhesive. Thus, it is important for the wood products industry to consider the future supplies of adhesives and the impact on future adhesive cost. Figure 2.2 shows the price differences for phenol (fluctuation) in Europe, United State and Asia, from February to May 2015.

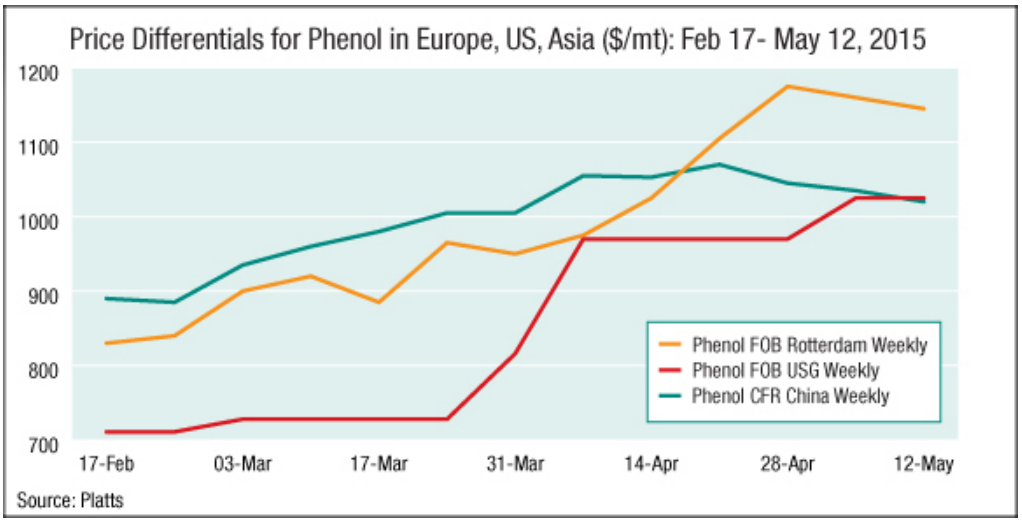

Figure 2.2: Price differences for phenol in Europe, United State and Asia (Platt, 2015).

2.2 Application of phenolic resins

The global phenolic resin market is expected to reach an estimated value of $13.3 billion by 2019 (PRNewire, 2015). One of the major drivers of phenolic resin market is the demand for heat resistance, better corrosion resistance, and chemical resistance materials. Increasing use of fire retardant materials in construction and furniture industry also increases the demand of phenolic resin. Figure 2.3 shows the world consumption of phenolic resin in 2014, whereby United State, China and Western Europe experienced the largest growth in the application of phenolic resin. High volume markets such as plywood, laminates, insulations and molding compounds continue to use huge amount of PF resin (IHS, 2014). The main applications of phenolic resin consist of composite, laminates and wood composite adhesives.

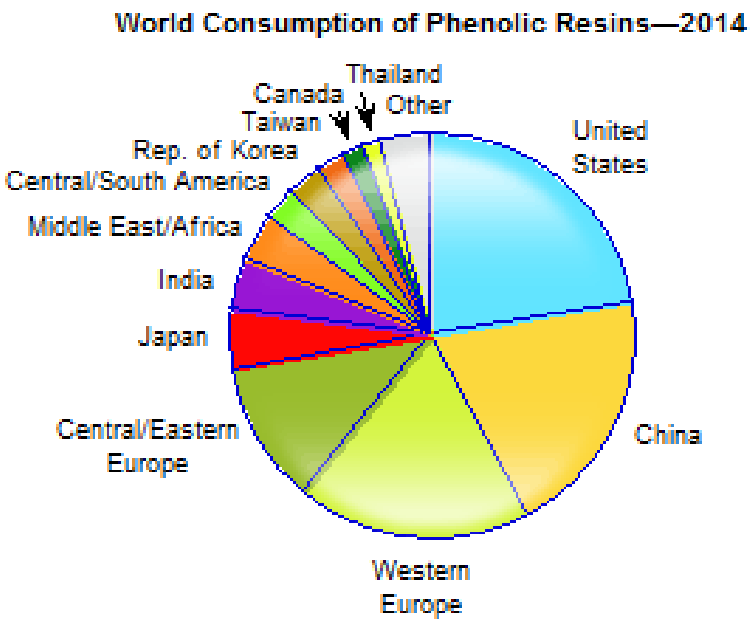

Figure 2.3: World consumption of phenolic resin in 2014 (IHS, 2014)

Phenolic composite materials cover a wide range of industries including infrastructure, marine, aerospace, aircraft, mass transit and defense but phenolic resins cover only 4-5% of the total composite resins worldwide market. However, phenolic resins have excellent flame retardant, heat and chemical resistance, electrical non-conductivity characteristics, low density, good thermal insulation, outstanding durability and ease of formability (Taylor, 2010).

Laminates are produced *via* impregnation of phenolic resins with various types of substrates such as glass fabric, cotton or paper as the core layer for the production of decorative and technical laminates. Molded laminate for industries uses fabric impregnation which consists of fiber impregnation for fiber reinforced plastic (FFP). Paper substrate is used in the impregnation of paper for electric laminates. However, these kinds of laminates are out of trend compared to the latest trend of paper electrical

laminates. Phenolic resin is also used for structural wood-based composites such as plywood, oriented star and board (OSB) and laminated veneer lumber (LVL). Most of the wood-based composites around the world especially in North America and Japan are phenol formaldehyde (PF) and resorcinol-phenol formaldehyde (PRF) resin systems as binders. Meanwhile, for South East Asia and China, melamine-urea formaldehyde (MUF) becomes the dominant choice because of their higher tolerance of veneer moisture content variations (Gomez-Bueso and Haupt, 2010).

2.3 Plywood manufacturing in Malaysia

Plywood is a panel, produced from sheets of veneer called plies which are bonded with adhesive *via* hot-pressing. Plywood are assembles in odd number of layers which are arranged in perpendicular grain order (Youngquist, 2012). In general, odd-numbered layers including the outer layers are oriented parallel to the long dimension of the panel to equalize the strain, minimize the dimensional change and reduce splitting. Plywood bonded with PF resin is commonly used for exterior application such as construction. However, for interior application, UF and MUF are favored due to the health issue which is related to the formaldehyde exposure.

Malaysia is one of the wood suppliers of wood-based products especially to Japan, Taiwan, Singapore and Middle East. According to the Malaysian Timber Industry Board, Malaysia is the leader for the production and export of veneer, tropical log wood and plywood (Malaysian Timber Industries Board, 2015). Many studies on biomass have been carried out to reduce the consumption of petroleum-based phenol

(Alma and Basturk, 2006). Biomass is the leading candidate because it is the only source that has fixed carbon, renewable and abundant.

2.4 Research of oil palm empty fruit bunch

One of the most important agricultural industries in Malaysia is palm oil refinery. According to the statistic given by the Malaysian Palm Oil Board (MPOB, 2014), the palm oil plantation produced a huge quantity of biomass waste in the form of palm kernel shell (PKS), palm oil mill effluent (POME) and empty fruit bunches (EFB). The waste of empty fruit bunches (EFB) were estimated around 70-80 million tonnes per annum, which are not well-utilized (MOPB, 2014). EFB does not contain chemicals or mineral additives but it is saturated with water, caused by the biological growth combined with the steam sterilization at the mill. Hence, pre-processing of EFB is required to eliminate around 67% of the moisture content.

Many studies have been conducted to use this renewable resources as raw material such as in polymer blended composite manufacturing (Rozman *et al*., 2004), cellulose (Umi Kalsom *et al*., 1997) and chemical productions (Rahman *et al*., 2007). In addition, the OPEFB is also used to produce medium density fibreboard (MDF), panels and composite boards (Ridzuan *et al*., 2002; Norul Izani *et al*., 2013) and bio-plastic (Salim *et al*., 2012). Since oil palm empty fruit bunch (OPEFB) is in the category of fibrous crop agriculture residues, OPEFB can also be converted into pulp (Wan Rosli *et al*, 2009). The high content of α-cellulose in this lignocellulosic waste also makes it a potential raw material for applications in the paper manufacturing industry (Akamatsu *et al*., 1987; Khoo and Lee, 1991; Wan Rosli *et al*., 1998). However, the pulp and paper

industry normally would burn the lignin that is dissolved in the black liquor for energy generation (Garcia *et al*., 2009; El Hage *et al*., 2009). The lignin which has been separated from hemicellulose and cellulose during the pulping process can be utilised as starting material, due to its variable functional groups. These functional groups provide tremendous potential reactive sites for chemical and biochemical modification.

In 2003, the first palm oil-based pulp and paper mills in the world, located in Sabah, Malaysia was established by the Forest Research Institute Malaysia (FRIM) and Advanced Borneo Sdn. Bhd. to manufacture pulp and paper. This is a potential route for future pulp and paper industry which indirectly helps to reduce the deforestation rate in the country. However, the pulping process also generates huge amount of black liqour waste, extracted for lignin to be used as biomaterials, fuels, animal feed or crops cultivation (Lora and Glasser, 2002). Lignin has wide potentials due to its high hydrophobicity, low glass transition temperatures, low molecular weight polydispersity with a variety of functional groups in its molecular structure (Vazquez, 1999). Table 2.1 shows the chemical composition of the oil palm biomass. OPEFB shows the highest lignin percentage compared to oil palm frond and oil palm trunk.

Table 2.1: Oil palm biomass chemical composition

Composition	Oil palm biomass chemical composition (wt%)		
	Empty fruit bunch	**frond**	**trunk**
Cellulose	43 – 65	40 – 50	29 – 37
Hemicellulose	17 – 33	34 – 38	12 – 17
Holocellulose	68 – 86	80 – 83	42 – 45
Lignin	13 – 37	20 – 21	18 – 23
Xylose	29 – 33	26 – 29	15 -18
Glucose	60 – 66	62 – 67	30 – 32
Ash	1 – 6	2 – 3	2 – 3

2.5 Lignin

Lignin is the major secondary cell walls and exists in all vascular plants, representing about 15 to 30% of the dry mass of wood which plays an important role in the transportation of water and nutrients because lignin is water resistant (Rohella *et al*., 1996). Lignin is a complex, cross-linked natural phenolic polymer and provides mechanical support for the plant, keeping them from collapsing. It waterproofs the cell wall which enables the transport of water and solute through the vascular system and protects against attack by microorganisms (Buranov and Mazza, 2008; Bonawitz and Chapple, 2010). Lignin is characterized by its rigidity, high strength, impact strength and resistance to UV light. The nature of the lignin polymerization reactions results in the formation of a three-dimensional, highly-branched, interlocking network of infinite molecular weight. Figure 2.4 is a schematic representation of a softwood lignin

proposed by Adler (1977) and later modified by Karhunen *et al*. (1999). This lignin model (Figure 2.4) does not depict the actual structure of lignin but instead, it serves as a tool to visualize the linkages and functional groups in lignin. The phenylpropane (C_9 or C_6C_3) units in lignin are connected by C-C and ether (C-O-C) linkages. However,there are many researches been conducted to identify the degradation products of lignin (Sarkanen and Ludwig, 1971; Adler, 1977; Lewis and Yamamoto, 1990; Argyropoulos and Menachem, 1998; Jung and Himmelsbach, 1989; Karhunen, 1999 and Allen, 2000).

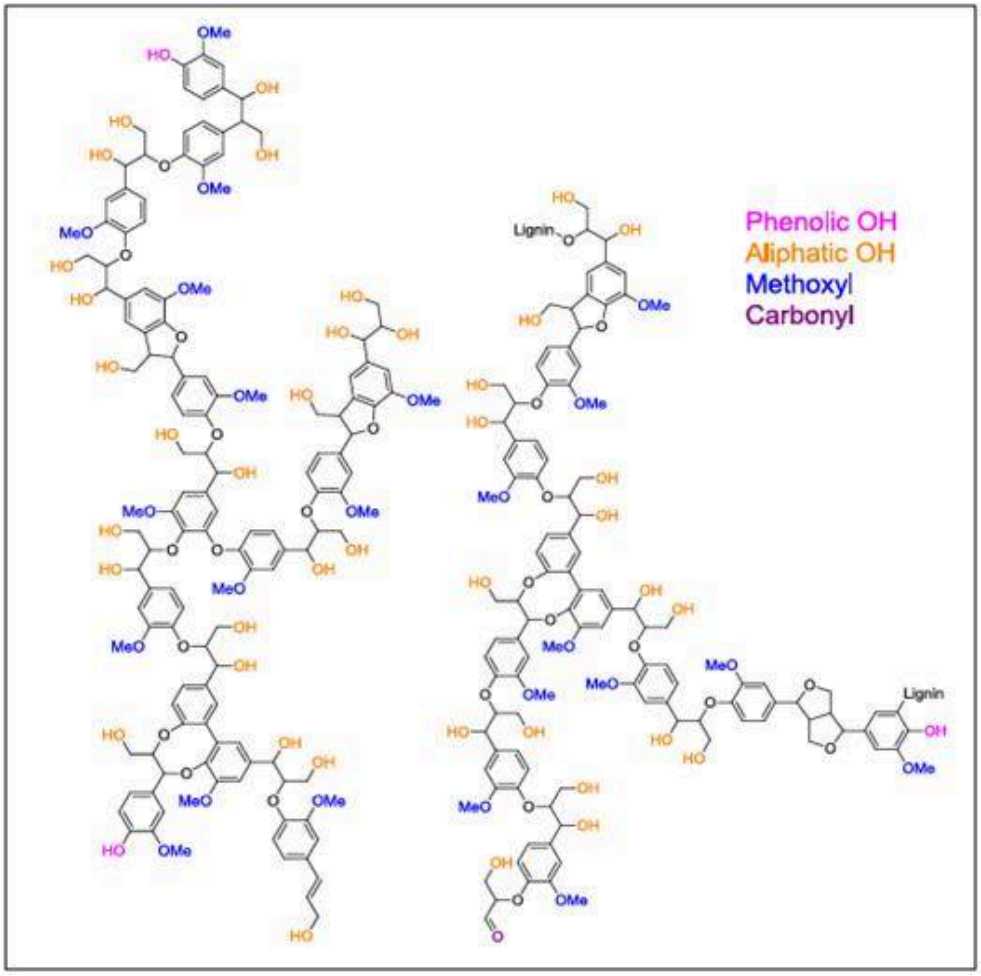

Figure 2.4: Chemical structure of lignin (Brunow, 2001)

Lignin is an amorphous polymer built up by oxidative coupling of three major units namely *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol as shown in Figure 2.5. These monolignols are incorporated into lignin in the form of the phenylpropanoids of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), respectively. In general, softwoods consist of guaiacyl lignin, composed of coniferyl alcohol monomers while hardwoods consist of guaiacyl-syringyl lignin, composed of coniferyl and sinapyl alcohols monomers. Grasses consist of graminaceous lignin composed of *p*-coumaryl alcohols (Hatakeyama *et al*., 2002; Koullas *et al*., 2006; Silva *et al*., 2009; Zakzeski *et al*., 2010).

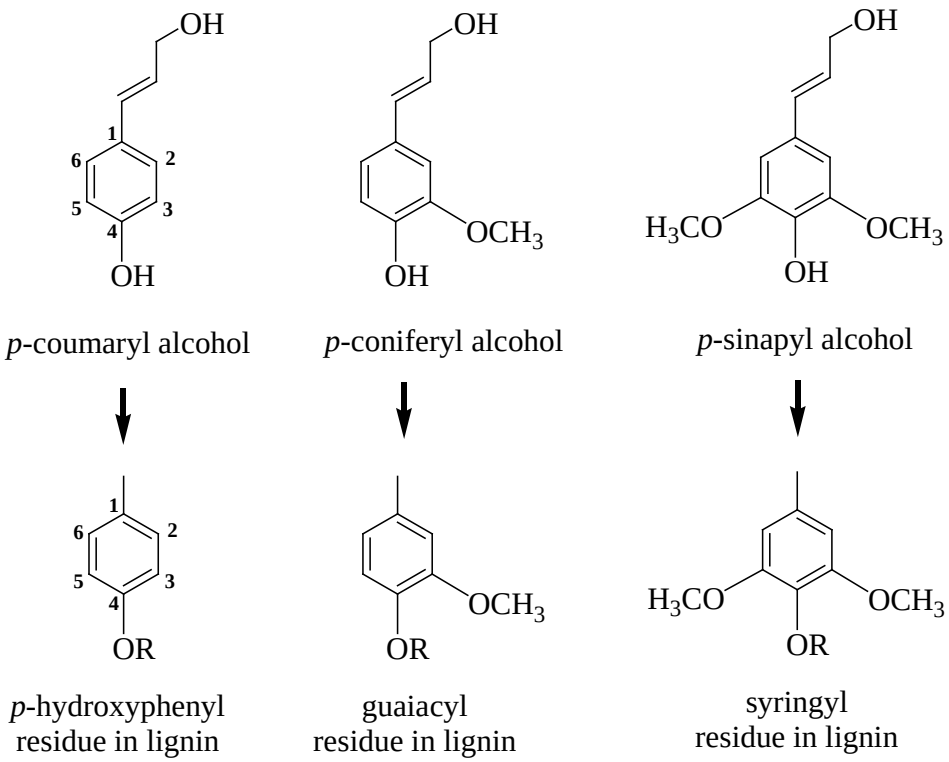

Figure 2.5: Three major phenylpropanoid units of lignin consist of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl

A variety of functional groups in lignin facilitate this natural polymer to undergo some chemical modifications. Studies have shown that some parts of lignin resemble phenol functional groups, making this an attractive material for substitution in wood adhesive resin (Vazquez *et al.*, 1999; Alonso *et al.*, 2005). Despite all the studies being conducted, the chemical and biological mechanisms of lignin are still not completely understood (Boerjan *et al*., 2003; Ralph *et al*., 2007).

The lignin which has been separated from hemicellulose and cellulose during the pulping process can be utilised as starting material, due to its variable functional groups. These functional groups provide tremendous potential reactive sites for chemical and biochemical modification. The lignin macromolecule also contains a variety of functional groups that have an impact on its reactivity. Lignin mostly contains the methoxy groups, phenolic hydroxyl groups, and few terminal aldehyde groups. The effectiveness of lignin depends on these functional groups, which varies depending on the extraction process. Only a small portion of the phenolic hydroxyl groups are free since most are linked to the neighboring phenylpropane. Carbonyl and alcoholic hydroxyl groups are incorporated into the lignin structure during enzymatic dehydrogenation. The common linkages in softwood lignin which connect the phenylpropane units are shown in Figure 2.6 and the proportions of these linkages are summarized in Table 2.2.

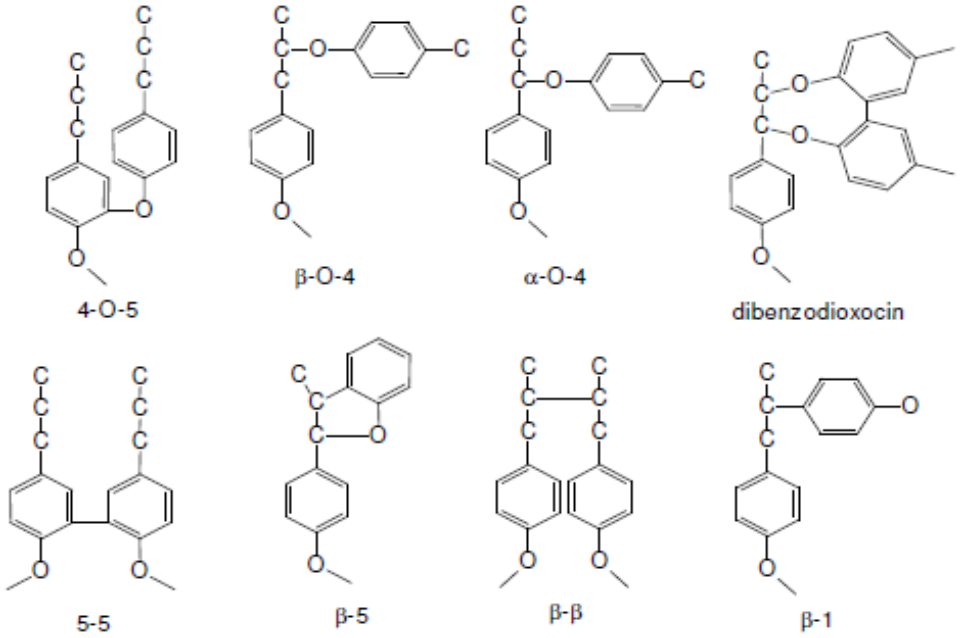

Figure 2.6: Main linkages found in softwood lignin (Karhunen *et al.*, 1995a; Karhunen *et al.*, 1995b)

Table 2.2: The abundance of some of the functional groups found in softwood lignin (Karhunen, 1999).

Linkage	**Dimer Structure**	**Percentage (%)**
β-O-4	Phenylpropane β-aryl ether	45-50
β-5	Phenylcoumaran	9-12
5-5	Biphenyl	15-25
5-5/α-O-4	Dibenzodioxicin	10-15
4-O-5	Diaryl ether	4-8
β-1	1,2-Diaryl propane	7
β-β	β-β-linked structures	3

In general, the solubility of lignin depends on the percentage of the functional groups whereby most types of lignin are soluble in alkaline solution due to the ionization of the carboxyl and hydroxyl groups. It was reported that the phenolic hydroxyl groups are free to form the neighbouring phenylpropane linkages, whereas others form the ether linkages (Henriksson, 2007). Lignin with phenol content is important due to its reactive sites in the structure which can lead to modifications, to be used especially in wood industry. By understanding the polymerization reactions, the cross-linking of lignin can be achieved through radical coupling reaction and condensation reaction. The frequency of some common functional groups found in ligninis illustrated in Table 2.3.

Table 2.3: Functional groups in softwood lignin, per 100 phenyl propane units

Functional Group	**Abundance per 100 C9 units**
Carbonyl	10-15
Benzyl alcohol	15-20
Phenolic hydroxyl (free)	15-30
Methoxyl	92-96

2.6 Pulping process

Chemical pulping is a process of removing lignin from wood to produce soluble fragments of the polymer (delignification). The removal of lignin allows individual fibers to be freed from the wood matrix through chemical degradation. The variations in the types of pulping materials and pulping conditions produce different lignin

properties. Minimizing the damage to the cellulosic portion of the fibers is important to maintain the strength of the lignin. Since lignin is embedded between cellulose and hemicelluloses (Figure 2.7), chemical pulping must be able to remove lignin from the middle lamella through chemical degradation, while minimizing damage to the cellulosic portion of the fibers to maintain the strength.

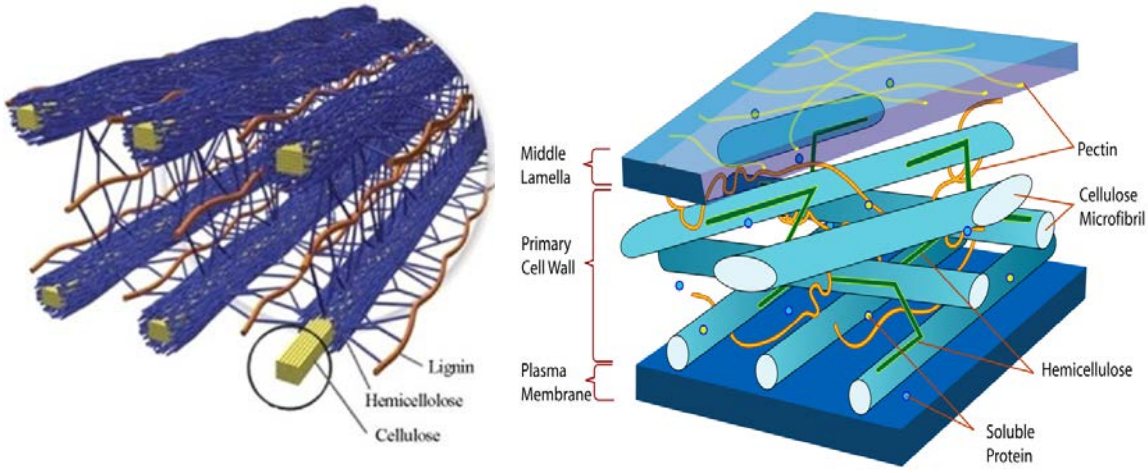

Figure 2.7: Location of lignin (Doherty *et al*., 2011)

The chemical pulping (delignification) occurs in two different methods – alkaline (kraft, soda) or acidic (sulfite) pulping process. In 1854, Hugh and Burgess developed and patented an alkaline pulping process which involved treatment of wood shavings with sodium hydroxide under elevated temperature conditions. Since the source of sodium hydroxide was from caustic soda, this alkaline pulping process was called the *soda process*. Later, in 1879, C.F. Dahl developed the sulfate or *kraft process* by replacing the sodium carbonate or soda ash with sodium hydroxide and sodium sulfide (white liquor) at 160-180°C with pH above 12. The hydroxide and hydrosulfide anions react with lignin during the kraft cook. The alkaline attack causes fragmentation

of lignin into lower molecular weight segment, which are then reacted with the thiol generated by sodium sulfide to form thiolignins which are soluble in strong alkali and can be precipitated upon acidifications. The lignin solubility in the cooking liquor is increased by cleavage of the linkages that hold the phenylpropane units together, thereby generating free phenolic hydroxyl groups. The most prevalent degradation reaction during kraft pulping includes the cleavage of α-aryl ether and β-aryl ether bonds which increases the amount of phenolics hydroxyl groups.

The pulp from this kraft pulping process is stronger and dark in color. The kraft process predominates because of its stronger pulps, insensitive to the presence of bark and high amounts of extractives, and adaptable to both hardwood and softwood tree species. The kraft process requires shorter cooking times with efficient recovery of pulping chemicals and the production of heat and valuable materials from by-products. However, the disadvantages of the kraft pulping are it is expensive, needs high reaction temperatures, low pulp yields, generates the foul odor from the degradation products, and the dark color of pulps (Smook, 1992). Overall, about 85-95% of the lignin present in wood is dissolved into cooking liquor. The black liqour is the waste liqour that is released after the kraft pulping process is completed. It contains most of the cooking chemical and the dissolved EFB substance including lignin, organic acids, hemicellulose and other compounds.

Kraft delignification modified the structure of lignin in two different ways to enhance its dissolution. The first is to degrade the lignin into smaller units by cleaving the inter unit linkages. The second is to introduce the hydrophilic groups into the polymer and to cleave the fragments, making the lignin more soluble in the cooking

liquor (Gierer, 1980). Cleavage of linkages with phenylpropane units generates free phenolic hydroxyl groups, which increases the hydrophilicity of the lignin and lignin fragments. Thus, the solubility of the lignin in the cooking liquor is increased. Meanwhile, the carbon-carbon linkages, being more stable are able to survive the kraft pulping process (Sjöström, 1993). During cooking, more than 95% of β-O-4 linkages in the lignin structures are hydrolyzed and lignin is degraded into fragments that are soluble in the alkaline solution (Gellerstedt and Zhang, 2011).

The interest in lignin to be used as starting material for the formulation of durable adhesive is due to its phenolic groups with repeating phenyl-propane units combined in various ways. This kind of material is expected to react with formaldehyde in a manner similar to that exhibited by phenol in a PF resin. Thus, it invites research into the formulation of lignin-based phenolic resin.

2.7 Phenol formaldehyde synthesis

Two main classes of adhesives have been developed depending on the reagent ratios and catalyst type, which are novolac and resole. Novolac are produced from acid catalyzed polymerization using excess phenol while resoles are produced from base catalyzed polymerization using excess formaldehyde. The manufacture of wood-based composites utilizes mainly the resole type (Robert, 1994).

2.7.1 Novolac type of phenolic resin

Novolac resins are produced by using acid catalyst at a molar ratio of formaldehyde to phenol of less than one (<1). The chemical structures of novolac resin do not contain methylol reactive groups and without the hardening agent, no reaction occurs between novolac molecules at high temperature. To complete the resinification, further addition of formaldehyde is required to enable the crosslinking process.

Phenolic ring is less reactive and act as a nucleophilic center in the acidic condition in the presence of hydroxyl group and protonation tends to occur in the phenol ring as shown in Figure 2.8. Aldehyde is protonated in the presence of acid catalyst. Protonated aldehyde forms more effective electrophile. Substituition reaction proceeds slowly, and the process of condensation occurs as a result of further protonation. The benzyl-carbonium ion formed serves as a nucleophile, as shown in Figure 2.8

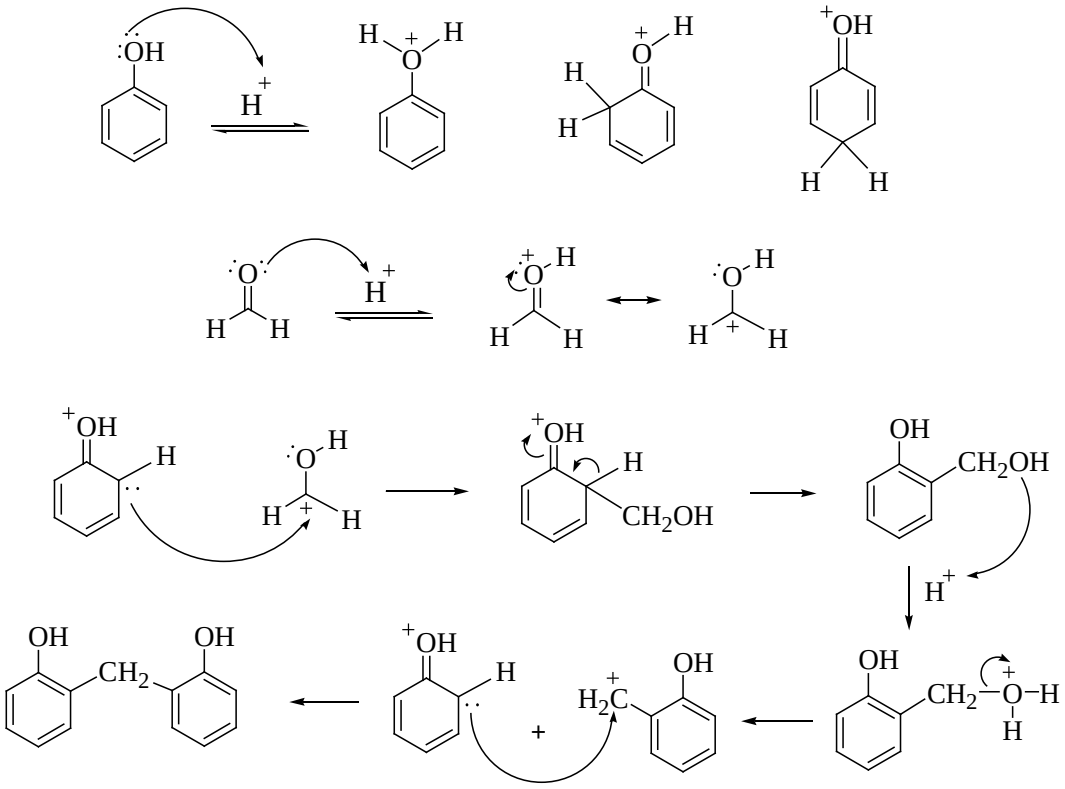

Figure 2.8: Mechanism reaction of the formation of benzyl-carbonium

2.7.2 Resol type phenolic resin

Resols are obtained under alkaline catalysis with an excess of formaldehyde. It contains reactive methylol groups which enable the resin to cure by itself when heated, forming large molecules without any hardening agents. The common F:P molar ratios is between 1.0 and 3.0 (Knop and Pilato, 1985). Metal hydroxide of sodium and potassium are commonly used as catalyst. Industrial resoles are usually manufactured by cooking the reagent from 1-8 hours at temperature below 100°C. Water is used as solvent so that the final resole solid content lies in the range of 40-60% (Pizzi, 1996).

PF resol polymers are formed through two reaction steps. The first step is methylolation or hydroxymethylation, which adds formaldehyde to phenol to form